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Development and Applications of Continuous-Wave Cavity Ring-Down Spectroscopy

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Abstract Continuous-wave cavity ring-down spectroscopy (CW-CRDS) (using continuous-wave lasers) is now in widespread use for the sensitive detection of a range of different trace-gas species, including water vapor as a very important trace contaminant in many gases. It has also now been applied to monitor trace water vapor in a range of matrix gases, including those that are corrosive and have the potential for spectral interference with the target water-vapor species. The developments that have been carried out to achieve this will be discussed, and some of the applications, covering single sensors and multi-head sensors, will be presented. One limitation of the current sensor technology is that it uses mirrors that are highly reflective over a very restricted spectral range, and this limits a given sensor to the measurement of one or two gaseous species. Measurements of other species require the mirrors to be changed, as it is not currently practical to obtain mirrors with the required high reflectivity that also cover a large spectral range. The development of a new type of ring-down cavity that uses uncoated reflective optics, and which can be used from the ultraviolet to the infrared spectral regions, is presented. Examples of industrial and scientific applications are also presented.

Keywords Industrial processes · Monitoring · Ring-down spectroscopy · Water vapor

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1 Introduction

Water vapor is an important contaminant in a wide range of high-purity gases. It causes detrimental effects in a number of industrial and commercial processes, such as chemical vapor deposition in semiconductor manufacturing, photolithography for the production of light-emitting diodes, the preparation of accurate calibration gas mixtures, and the transport of natural gas through pipelines. A range of well-established methods are in use for real time on-line measurements of trace concentrations of water vapor in inert gases, including certain spectroscopic techniques, although some of these are limited in their detection sensitivities and/or have slow response times. However, there are pressing needs to monitor trace water-vapor concentrations at extremely low levels in a range of corrosive and reactive gases (e.g., ammonia, hydrogen chloride, phosphine). These measurements are generally difficult to perform because the corrosive nature of the matrix gases affects the sensors, and they are also difficult to measure spectroscopically because of interferences arising from the spectrum of the bulk gas itself.

This paper discusses recent developments that have enabled the practical realization of commercial trace-gas measurements for a range of gases including water vapor, using the technique of continuous-wave cavity ring-down spectroscopy (CW-CRDS afterward in this paper abbreviated to CRDS), generally operated in the infrared spectral region. Examples are given of applications to monitoring specialized industrial processes. These CRDS instruments are also capable of providing multi-point trace-gas sensing of industrial processes and of providing multi-species monitors, including water vapor, but also a range of other gaseous species as listed at the end of Sect. 4.

A recent development involves a new and innovative optical system for use with the CRDS spectrometer so as to extend the spectral range and coverage of the technique. This is discussed, and some examples of the potential applications are listed. A brief overview of the scientific principles of the CRDS technique is, however, given first.

2 Principles of Cavity Ring-Down Spectroscopy

CRDS has its origins in the measurement of the reflectance properties of very high reflectivity optical mirrors for use with lasers and similar devices. The CRDS technique was first used for spectroscopic measurements by O'Keefe and Deacon [1]. Using this technique, optical absorption is determined by a measurement of a decay time of optical radiation in a cavity, rather than the conventional method that uses measurements of optical intensity. The theoretical background to this has been published [2]. A simplified schematic of the CRDS technique is shown in Fig. 1.

There are three essential components to the technique—a laser as a source of optical radiation, an optical cavity formed with two highly reflecting mirrors, and an optical detector. The optical cavity is excited (filled) with radiation from the laser, and this cycles around the cavity up to tens of thousands of times due to the high reflectivity of the mirrors. When the laser radiation is rapidly switched off, the intensity of the radiation in the cavity decays exponentially with time. A small amount of this radiation leaks out of the cavity each cycle, and this is measured on the detector. This exponential

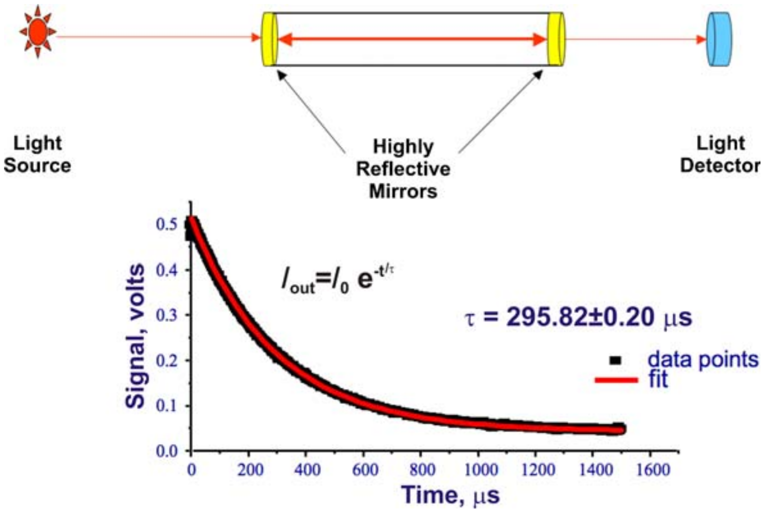

Fig. 1 Principles of the CW-CRDS technique

decay, typically lasting several hundred microseconds, corresponds to an 'effective' path-length in the cavity of typically 80 km. Thus, as the detection sensitivity in an optical absorption technique is generally proportional to the optical path-length, this translates into a very small detection limit. This decay rate (known as the ring-down time) arises from optical losses within the cavity. When the cell is empty, or does not contain a gas that absorbs at the laser wavelength, the ring-down time τ_{empty} is generally determined by the reflectivity of the mirrors (see Fig. 1). (The above technique of continuous-wave cavity ring-down spectroscopy has been patented.)

In practice, τ_{empty} is not measured with an empty cavity but is measured at a wavelength where there is negligible absorption from the gas in the cavity. This is shown in Fig. 2. Then, when the laser is tuned in wavelength to the peak of a specific absorption line of the selected gas (in this case, water vapor), the second measurement of ring-down time, $\tau(\nu)$, at the wavelength of this peak (Fig. 2), is shortened in a manner that is related to the amount of gas in the cavity and the strength of the selected spectral line, in keeping with Beer's law.

The measurement of these two exponential decays enables the concentration of the trace gas in the cavity to be determined, as given below:

$$\text{First measurement: } \tau_{\text{empty}} = d/c(1-R) \tag{1}$$

$$\text{Second measurement: } \tau(\nu) = d/c(1-R+\sigma(\nu)Nd) \tag{2}$$

$$\text{Calculate concentration: } N = (1/\tau(\nu) - 1/\tau_{\text{empty}})/c\sigma(\nu) \tag{3}$$

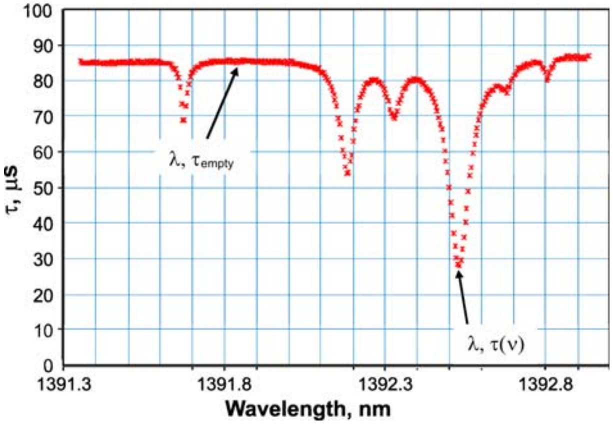

Fig. 2 High-resolution infrared spectrum of water vapor produced by the CW-CRDS technique, showing the ring-down measurements made

where τ_{empty} is the cavity ring-down time at a wavelength where there is no significant absorption of the gas; $\tau(\nu)$ is the cavity ring-down time at a wavelength that is tuned to a peak absorption line of the gas; d is the geometric distance between the two mirrors providing the ring-down cavity; c is the velocity of light; R is the reflectivity of the pair of mirrors providing the cavity ring-down; $\sigma(\nu)$ is the absorption cross section of the spectral line of the gas at wavelength ν; and N is the concentration of the gas within the ring-down cavity.

3 Advantages of the CRDS Technique for Measurements of Water Vapor and Other Trace Gases

There are a number of advantages of the CRDS technique when compared with other trace water-vapor measurement techniques. These have been given previously [3], but are summarized below:

- The components in contact with the gas stream being measured have a small volume and can be constructed of suitable materials so that they can be rapidly dried from high concentrations, resulting in a fast speed of response.
- The effective absorption path-length of the cell can be 10^5 times its actual mechanical length, resulting in very small detection limits.
- An individual measurement can be made in typically much less than one second.
- Very high spectral resolution provides very high specificity, minimizing cross-interference effects from other trace species present, and from the matrix gas.
- It is capable of determining the concentrations of trace water vapor in a wide range of matrix gases, including corrosive ones, and those with spectral features in adjacent and overlapping spectral regions to that of water vapor.
- The measuring system is only responsive to the gas within the cell and not to that in all the surrounding components of the instrument.
- The system is constructed of materials that operate with corrosive or reactive gases.

- The detection sensitivity is not affected by intensity variations in the optical source, and present in all laser systems, unlike more conventional spectroscopic methods.
- A wide dynamic range of concentration measurements are achievable from sub-parts per billion to around 100 parts per million, selectable by choice of the optical cell length.
- The technique makes use of reference spectra with known optical properties that enable accurate measurements to be made continuously without regular calibrations while it is being used for on-line monitoring. In addition, the long-term stability and the spectral resolution of the CW-CRDS technique means that it may also be used as a transfer standard [3].
- It has a simple robust design with no moving parts, which makes it reliable, and it thus has a low cost of ownership.

4 Applications to Trace Water-Vapor Measurements

The CRDS technique has been used for a wide range of scientific, technical, and industrial applications, many involving the monitoring of trace water vapor, including:

(i) The presence of trace levels of water vapor within the process gases that are used for semiconductor epitaxial growth is detrimental to the opto-electronic properties of the final devices, and to the yield of satisfactory devices in the production process. Sensitive specific analytical on-line techniques are required to monitor the purity of the process gases and to detect unacceptable contamination. The CRDS technique has demonstrated capability to monitor trace water vapor in a wide range of corrosive and toxic process gases—including PH_3, HCl, HBr, NH_3, AsH_3, and CF_4, [5–7] using the low-pressure CRDS technique to minimize interference (as discussed above), down to ppb levels.

(ii) The development and application of photolithography used for semiconductor processing at wavelengths shorter than 190 nm increases the potential for photo-induced reactions with any water-vapor contamination. This leads to irreversible oxidation of the lithographic optics. Such systems demand ultra-pure process gases and clean vacuum environments, and these give rise to the requirements for monitoring trace water vapor down to levels below 1 ppb.

(iii) High-purity bulk ammonia gas, for example, is used in the manufacture of gallium nitride-based high-brightness blue and white light-emitting diodes (LEDs). Similar issues arise in the production of other types of LEDs and liquid-crystal displays. Trace water-vapor impurities in the ammonia can cause large reductions in the yield of the LEDs, for example, during the process of metal organic chemical vapor deposition (MOCVD). Thus, bulk-gas suppliers and LED manufacturers need to detect low ppb levels of H_2O in ammonia and other bulk gases. This is readily achievable with low-pressure CRDS, when the infrared spectral lines of the ammonia gas become narrow, and it becomes practical to monitor trace H_2O levels in the presence of these spectral features, without significant cross-interference effects. Similar issues arise in the production of other types of LEDs and liquid-crystal displays.

(iv) There are rigorous demands for the measurement of trace impurities in specialty gas manufacturing, and in cylinder-gas quality control. Examples include the detection of trace water vapor in nitrogen and synthetic air matrix gases employed to prepare low-concentration gas mixtures (SO_2, NO_2, H_2S, etc.) used for environmental monitoring applications. The presence of trace water in these calibration mixtures severely impairs their concentration stability over time.

(v) Many industrial plants require that trace water vapor and other impurities are monitored at multiple points within the processes. This is regularly achievable with CRDS by the use of multiple optical sensing heads, connected to one electronic processing unit. This enables multiplexed measurements of the same or different trace species, at different locations within the plant.

(vi) The CRDS technique is extremely stable in its response to any given concentration of trace water vapor. It can therefore be used as a transfer standard to evaluate the consistency of national, and other, water-vapor calibration facilities throughout the world. Intercomparisons between national laboratories are now underway to harmonize the results obtained with these calibration facilities, and these are using the CRDS technique [4].

In addition to the above examples listing trace water-vapor measurements using the CW-CRDS technique, this technique has been developed and applied for monitoring an increasingly large range of other trace gases with high sensitivity and specificity, including H_2S, HBr, HCN, NH3, C_2H_2, N_2O, NO_2, and HCHO in different matrix gases, down to ppb concentration levels [5–7].

5 Verification of the Accuracy of the CRDS Technique

As noted above, the accuracy of the CRDS is determined by the spectroscopic data used in the calculation given in Fig. 2. There have been experiments to verify the accuracy of the technique, using facilities at national measurement institutes worldwide. One such verification of the CRDS results was against the primary low frost-point generator (LFPG) maintained at the National Institute for Standards and Technology (NIST), USA. The results obtained are shown in Fig. 3. It can be seen that they agree with each other to within about 3 % over the range from (0 to 1,000) parts per billion, that the CRDS technique is linear over this large dynamic range, and it has also been shown through a range of intercomparisons at national measurement institutes in the USA and Europe that the results obtained with the technique are stable over very long time scales, due to the fact that the technique utilizes accurate spectroscopic data [3].

6 Development of New Multi-species CW-CRDS Monitors

One of the limitations of the current sensor technology is that it uses mirrors (see above) that are very highly reflective, but this is achievable only over a very restricted wavelength range (typically a few percent of wavelength). This limits a given sensor to the measurement of one, or at most two, species. More recently, the CRDS technique

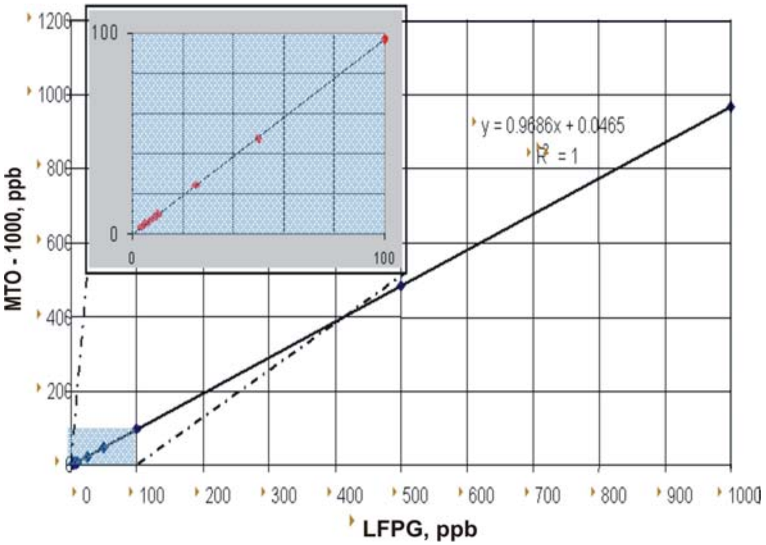

Fig. 3 Comparison of the Tiger Optics ML CW-CRDS system with the primary standard low-temperature frost-point generator at NIST, USA

has been developed using high-quality fused-silica prisms, configured into a stable ring-cavity optical resonator.

Total internal reflection within these prisms, together with the use of Brewster's angles to minimize Fresnel reflections, is employed to provide very high reflectivity across a broad wavelength region potentially covering the ultraviolet, visible, and near infrared. Figure 4 shows a schematic layout of this with the capability for multiple gaseous species detection. This optical cavity has been fully characterized with respect to its optical parameters, including:

- Fresnel losses at the prism faces;
- bulk scattering within the prism materials;
- diffraction losses;
- stress-induced birefringence within the prisms;
- optical leakages at the reflective internal surfaces; and
- dispersion of the prisms as a function of wavelength.

Figure 5 shows the calculated optical losses due to these effects as a function of wavelength across the infrared, visible, and ultraviolet spectral regions, demonstrating the capability to measure at a wide range of wavelengths.

In practice, the experimental realizations generally have lower losses than the calculations shown in Fig. 5, and cavity ring-down times corresponding to optical path-lengths within the CRDS system have been measured at >10 km in the near infrared. Different laser sources can be directed into the prism cavity by a number of means, including using fiber optics with optical fiber switches. Alternatively, for example, a single tunable-wavelength source may be used (see Fig. 5). The long path-lengths achievable, together with the broad spectral coverage, enable high-sensitivity detection and fast response for measurements of a broad range of gaseous species almost

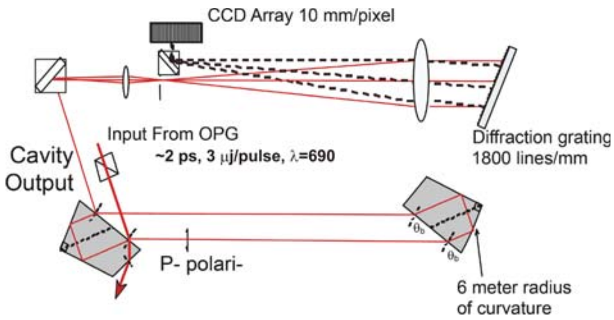

Fig. 4 Example of a configuration of a continuous-wave prism cavity ring-down system for multi-wavelength detection

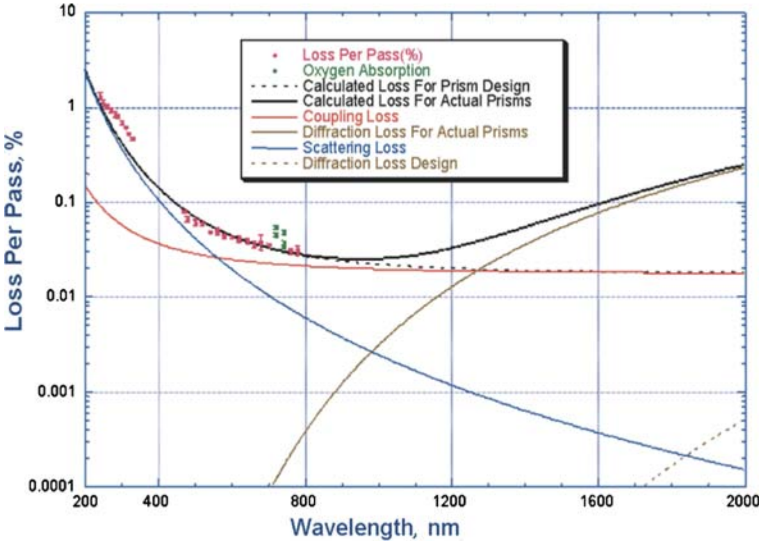

Fig. 5 Optical losses as a function of wavelength determined for a prism-based CW-CRDS system

simultaneously. Table 1 lists some of the species measurable with such a CRDS system, together with the wavelengths that could be employed, and the estimated detection sensitivities.

The above CW-CRDS technique using prisms for the optical cavity has been developed with funding from the US National Science Foundation, and is also covered by a patent owned by Princeton University and license exclusively to Tiger Optics LLC. The prism-cavity technique will be made available as a sensitive, accurate, and reliable instrument in the near future, to complement those already commercialized.

Table 1 Examples of gaseous species detectable using a CW-CRDS system having a broad wavelength coverage

Molecule		Near infrared		Mid infrared	
		λ (nm)	(ppb)	λ (nm)	(ppt)
Water	H_2O	1,390	0.5	5, 940	16.7
Carbon dioxide	CO_2	1,960	25.0	4, 230	1.1
Carbon monoxide	CO	1,570	250.0	4, 600	6.3
		2,330	4.2		
Nitric oxide	NO	1,800	500.0	5, 250	48.3
		2,650	8.3		
Nitrogen dioxide	NO_2	680	2.8	6, 140	25.0
Nitrous oxide	N_2O	2,260	8.3	4, 470	3.7
Sulfur dioxide	SO_2			7, 280	116.7
Methane	CH_4	1,650	5.0	3, 260	14.2
Acetylene	C_2H_2	1,520	0.7	7, 400	29.2
Hydrogen fluoride	HF	1,310	0.1		
Hydrogen chloride	HCl	1,790	1.3	3, 400	6.9
Hydrogen bromide	HBr	1,960	5.0	3, 820	60.0
Hydrogen iodide	HI	1,540	17.5		
Hydrogen cyanide	HCN	1,540	2.4	6, 910	100.0
Hydrogen sulfide	H_2S	1,570	166.7		
Ozone	O_3			9, 500	91.7
Ammonia	NH_3	1,500	6.7	10, 300	6.7
Formaldehyde	H_2CO	1,930	416.7	3, 550	70.0
Phosphine	PH_3	2,150	8.3	10, 100	51.7
Oxygen	O_2	760	650.0		

7 Potential Applications of Prism-Based Cavity Ring-Down Spectroscopy

As noted above, recent developments in the prism-based CRDS technique for multi-species monitoring allows a larger number of potential applications. Such a CRDS monitor may be designed to measure:

(a) Multi-species industrial process monitoring: Examples of current applications for trace water-vapor sensing are given in Sect. 4 above. On-line rapid specific monitoring of ethylene, and other volatile organic compounds, is required by the petrochemical industry to control industrial production processes.

(b) Analytical laboratory measurements: CRDS may be used as a multi-gas sensor for trace impurity measurements in many laboratory applications, where there is a requirement to analyze the purity of different matrix gases before use, including trace measurements of volatile organic compounds, oxygen, water vapor, formaldehyde, sulfur dioxide, and nitrogen oxides.

(c) Medical diagnostics: The detection of trace gases, such as acetaldehyde, ethanol, esters, and other volatile organic compounds, and their isotopes, on human breath, as well as for sensing of other gases such as nitrous oxide.

(d) Industrial emissions to the atmosphere: Applicable, for example, to monitoring a range of important gaseous pollutants that are difficult to measure with other techniques but are emitted to the atmosphere from industrial stacks, vents, and ducts—including NH_3, HF, HCl, HCHO, CH_4, and other volatile organic compounds.

(e) Monitoring ambient air quality: Existing instrumentation is already in use in the field for different ambient air quality monitoring, but it generally has a high cost of ownership and requires frequent calibrations. In addition, some gaseous pollutants are difficult to detect with the accuracy and detection sensitivity that is needed. Examples include measurements of the ambient concentrations of ammonia, formaldehyde, hydrogen sulfide, ethylene, and acetylene.

(f) On-line monitoring of vehicle emissions and the testing of new engines: As vehicle emission controls become more stringent, and the engines become more complex and cost effective to run, there are increased requirements for more sophisticated on-line engine diagnostic and management systems that have multi-parameter sensing. There are requirements for monitoring low concentrations of, for example, nitrogen oxides, hydrogen sulfide, methane, and other volatile organic compounds.

(g) On-line monitoring of natural gas species and contaminants: The processing and transport of natural gas is a complex process, and accurate measurements of the concentrations of many constituents are needed to ensure these are carried out efficiently. Incorrect measurements can lead to fiscal metering errors or to contamination of the transport pipes. There are requirements for specific on-line monitoring of water-vapor content in these in the presence of the complex range of species present in natural gas, and also for checks on the concentrations of other trace contaminants.

There are also a range of specialized scientific applications, including measurements related to an improved scientific understanding of atmospheric chemistry, environmental research, air pollution, and for climate-change purposes.

8 Summary

The technique of cavity ring-down spectroscopy is being applied to an increasing range of scientific, commercial, and industrial applications where there are requirements for monitoring trace concentrations of water vapor and other species, generally using high-reflectivity mirrors in the infrared spectral region. The CRDS technique has high sensitivity, specificity, and reliability, for continuous on-line monitoring. These monitors can make trace water vapor concentration measurements in a wide range of different matrix gases – inert (e.g., N_2, He, Ar), flammable (e.g., H_2, CH_4), and corrosive (e.g., HBr, HF, PF_3, NF_3). Multi-point and multi-species sensing is used. The CRDS technique has recently been developed using a prism cavity to enable near-simultaneous measurements across the ultraviolet, visible, and infrared spectral regions, and trace gas measurements have been carried out using this technique. This enables a much larger range of trace gases to be monitored, and for different applications.

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